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US ARMY RDECOM

U.S. Army Research, Development and Engineering Command

Ionic Additives for Electrochemical Devices Using Intercalation Electrodes

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

Inventor: Dr. Kang Xu

ARL 09-18

APPROVED FOR PUBLIC RELEASE

February 16, 2011

Technology Overview

This invention relates to an ionic additive technology that modifies the edge sites of a graphitic anode to ease Li^+ (lithium ion) transport. The invention greatly reduces power-robbing effects of "charge transfer" resistance.

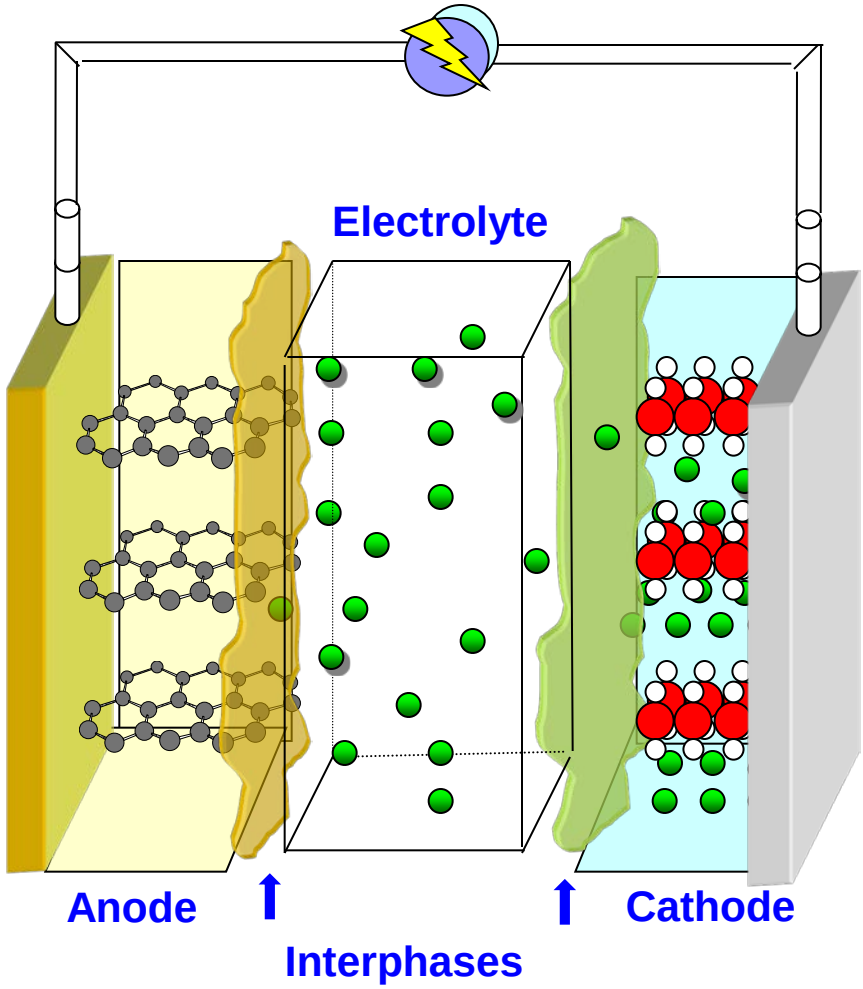
How Li Ion Battery works

- Li ion battery is an "intercalation" battery chemistry
- Graphite is the "universal" anode used in Li ion batteries
- Li^+ transport at graphite constitutes the most difficult step and it dictates the power density of a Li-ion device

The new ionic additives form a new interphase that facilitates Li^+ transport

- Reduces "charge-transfer" resistance by 2/3
- Activation energy barrier lowered to ~40 kJ/mol vs. current 60~70 kJ/mol
- Faster Li^+ movement = Higher Power Density

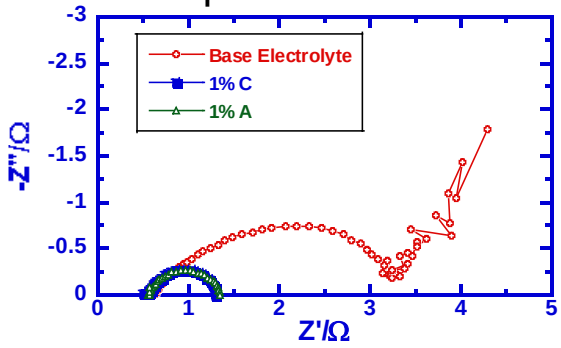
The additive material is easily available from commercial source, is low cost and has minimal impact on the existing battery manufacturing processes



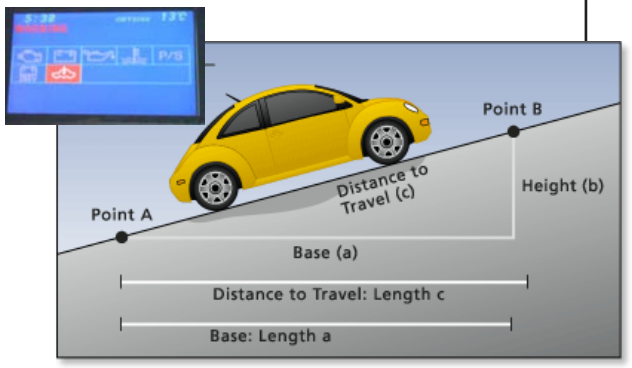
Technology Overview

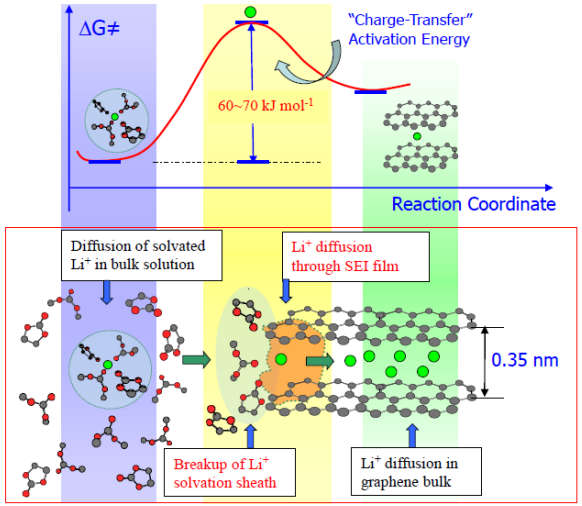
The innovation is part of a family of ionic additive compounds based on a salt with a cation (positive ion) that can be reduced into metal at > 1.0 V at intercalation sites. The result is graphite edge sites with "metallic" nature that are more receptive to the transport of Li^+.

- Current electrolyte usually results in ~60-70 kJ/mol energy barrier and > 3 Ω resistance at graphite/electrolyte interphase in a 0.97 cm^2 electrode
- < 1% additive of Ag^+, Cu^{2+} or Zn^{2+} salt dramatically improved both interphasial resistance (< 1.5 W) and activation energy barrier (< 40 kJ/mol)
- The metal clusters precisely targets the edge sites of intercalation electrode, leaving

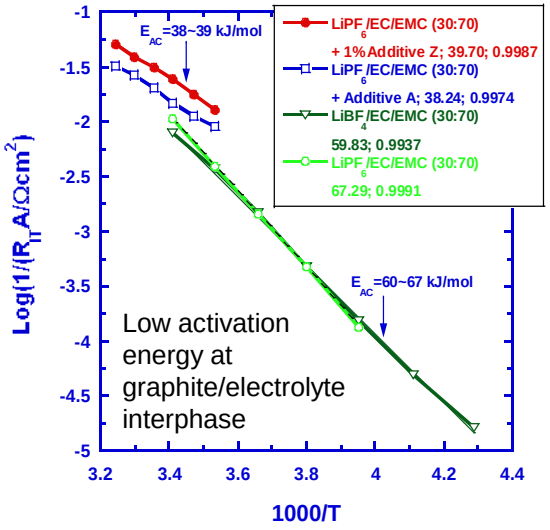


Activation energy barrier at graphite/electrolyte interphase





Low impedance at graphite/electrolyte interphase



Technology Advantages

Challenges addressed by the invention:

- Graphite is the “universal” anode most Li ion batteries
- However, the electrolyte/graphite interface is very resistive
- Previous attempts to address this resistive interface (e.g. metal coating) are difficult, expensive and “indiscriminate”

These additives in this invention pave a very simple but effective path for surface modification of graphite or any other intercalation electrode

- Specifically targets the “edge-sites” : Li^+ intercalation sites
- Achieves “nano-metallization” at the edge sites
- Effectively reduces the interphasial resistance
- Flexible and open system
  - Deposition potential of ionic additives tunable
  - Can be combined with the 5 V electrolyte technology

Easy access and inexpensive method to prepare

- Precursor materials readily available from commercial source
- Simple mix with state-of-art electrolyte

Technology Differentiation

Batteries used in electric vehicles (EVs), especially in hybrid power systems, require high power density

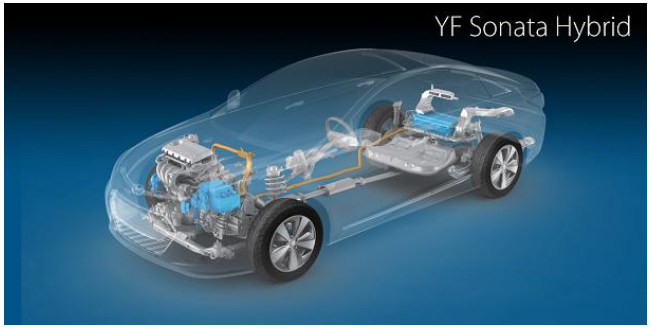
- to capture the regenerative energy only present during the 10 seconds scale
- To release the energy while accelerating

An ordinary graphite anode fails to rapidly capture such energy produced

- Slow Li^+ transport at edge site interphase doesn't allow capture or release of the energy on the required time-scale because of high resistance
- High resistance also leads to metal Li deposition
  - Service life shortened
  - Potential hazard: fire and explosion

This invention provides an easy and simple solution for a high power density graphitic anode

- Open system: accommodates various cathode chemistries
- Increased service life and safety
- Can be combined with 5 V electrolyte additives

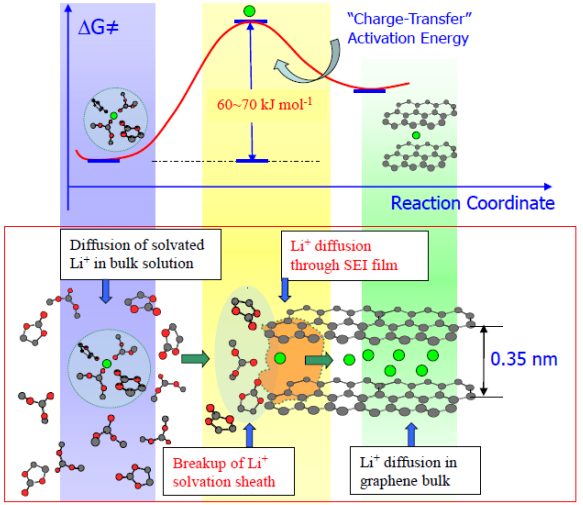


Technology Proof of Concept

Method of Preparation of Novel Additives

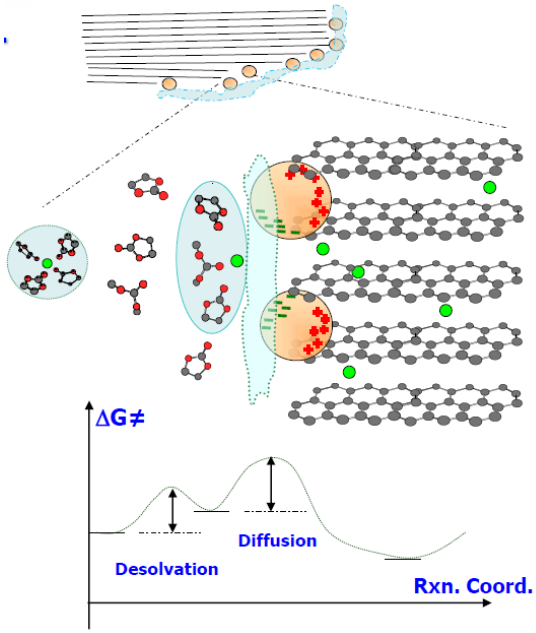
Simple electrolyte mixing in glovebox or dryroom

Coin cells assembled using industry standard electrodes



Energy barrier of Li^+-transport across the interphase at edge-sites of an intercalation electrode

Ionic additive of the invention introduces "metallic" nature that assists Li^+-transport



Military Applications

Military applications would significantly benefit from the improvement in commercial Li ion technologies

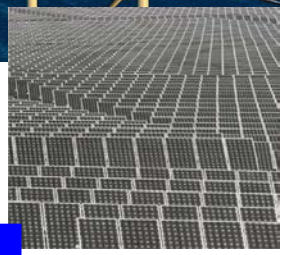
- Major Impact: Military HEV operation and “silence surveillance “ capability
- Reduction of logistic burden
- High power applications: EM gun/EM armor/Directed Energy Weapons

APU in various Military Vehicles

Commercial Applications

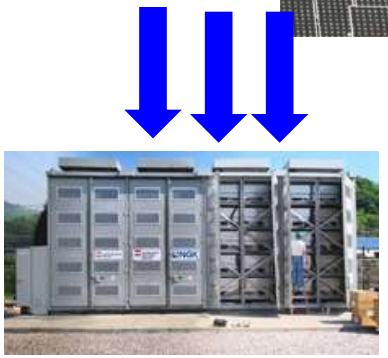
The invention can benefit a number of commercial battery applications, including

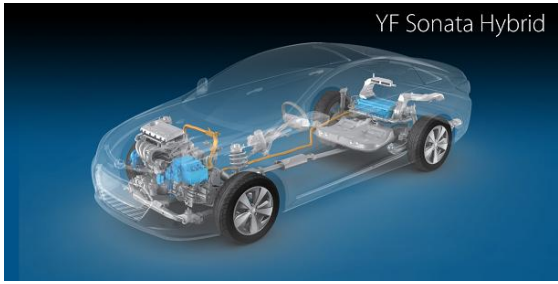
- Vehicle electrification applications (HEV/PHEV/BEV)
- Large-scale energy storage devices (grid-stabilization, load-levelling)



Additionally, the invention can benefit other applications that employ intercalation-type electrodes, including:

- Ultracapacitors
- Hybrid capacitors
  - The activated carbon could be modified to facilitate charge-accumulations at the electrolyte/electrode interfaces





Technology Agreements

A patent license and CRADA is sought.

– The current technology would benefit from a collaboration between the inventor team and the commercialization partner in order to speed the development to the market. This would most readily be done through a CRADA/patent license agreement. The inventor team is available to work with commercialization partner

• TRL 5 – Fully functioning battery prototypes using coin and pouch cell formats

•A patent application has been filed